Applied predictive thermodynamics (*ThermAP*). Part 2. Apatites containing Ni^{2+}, Co^{2+}, Mn^{2+}, or Fe^{2+} ions

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ABSTRACT

Apatites are minerals encountered in many fields including geochemistry, nuclear and environmental sciences as well as medicine. This ubiquity is likely related to the diversity of ion substitutions that the apatite structure can accommodate, making of it an excellent "ion reservoir" either in natural settings or for the intentional production of doped systems with tailored properties. Despite this widespread interest for apatite compounds, however, only few studies are dedicated to study their thermodynamic properties. Yet, their knowledge becomes necessary for assessing stability domains and understanding evolutionary trends in solution or upon heating, for example. Recently, the experimental thermodynamics of 33 phosphate apatite compounds (deriving from the composition $M_{10}(PO_4)_6X_2$) have been reviewed and their comparison allowed the development of the additive predictive model "*ThermAP*" (*Applied Predictive Thermodynamics*) capable of adequately predicting properties such as standard enthalpies (ΔH_f°), Gibbs free energies of formation (ΔG_f°), or entropies (S°) at T 298 K, for any composition involving ions among M^{2+} Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+} and X OH , F , Cl or Br . Although experimental data for apatites involving other divalent cations such as Ni^{2+}, Co^{2+}, Mn^{2+} or Fe^{2+} do not seem to be available, the exploration of apatites doped with these ions is appealing from a practical and fundamental viewpoint, for example for understanding geochemical events, or when using apatite precipitation for the elimination of metal cations from industrial wastewaters, or else for conferring magnetic properties to apatite systems in medicine. Based on multiple physico chemical correlations, the present contribution extends the additive predictive model *ThermAP* to Ni , Co , Mn(II) and Fe(II) doped apatites. It provides for the first time estimations of enthalpies, Gibbs free energies of formation and entropies, unveiling the general stability ranking Mn(II) apatite > Fe(II) apatite > Co apatite ⩾ Ni apatite. This additive approach also allows one to estimate these properties for any composition in view of enabling thermodynamic calculations for applicative or fundamental purposes.

1. Introduction

Apatites are ubiquitous minerals found in many domains, as was commented previously [1]. In particular, phosphate apatites deriving from the generic formula $M_{10}(PO_4)_6X_2$ represent an important subclass [2 4]. Whether for understanding natural phenomena such as biomineralization and geological phosphate rock formation/weathering, for explaining mineral evolutions upon immersion or heating, or else for optimizing industrial processes involving such compounds, the knowledge of their thermodynamic properties becomes a primordial prerequisite (besides adequate physico chemical characterization). Unfortunately, this thermodynamic aspect is sometimes disregarded, which can be concluded from the rather limited literature existing on this domain. In a previous recent work [1], the available reported experimental data on phosphate apatite end members, ranging from the 1950s to nowadays has been reviewed and compiled in a single reference document [1], giving an overview of standard formation energetics (ΔH_f° and ΔG_f°), entropy S° and molar heat capacity $C_{p,m}^\circ$. In that review work, the compilation of data for 33 phosphate apatite end members involving the ions Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, PO_4^{3-}, HPO_4^{2-}, OH^-, F^-, Cl^- and/or Br^-, then made it possible to quantify the "contributive" role of each of these ions in the energetics of apatitic compounds, thanks for a contributional additive model [1,5] that can be referred to as *ThermAP* for *Applied Predictive Thermodynamics*.

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In the present work, the idea was to expand this list of ions in phosphate apatite systems to the cations Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+}. Indeed, these ions may be found in some contaminated water from mines or in industrial waste waters, thus leading to pollution issues [6], and their precipitation in the form of a stable solid phase can then be seen as a clever removal process for depollution purposes [7,8]. In this field, the setup of permeable reactive barrier systems for groundwater remediation has in particular been developed [6], including using apatite as solid remediator [7,8]. Also, these ions exhibit specific electron features that may prove of interest in the design of magnetic apatite systems (e.g. for the magnetic guidance of doped nanoparticles towards a diseased tissue) [9] or for exploiting cathodoluminescence features. In the geochemical field, manganese is also known to be found in igneous, metamorphic and sedimentary apatites [10,11]. The possible precipitation of Mn , Ni , Co , or Fe containing apatites or sorption of these ions on apatite were also reported (see for example references [12 19]).

In the present contribution, I will first summarize the main aspects concerning the *ThermAP* additive thermodynamic model that was recently developed to evaluate the energetics of phosphate apatite compounds (the initial paper, reference [1], being considered as "Part 1" of the series of papers dedicated to the *ThermAP* approach). Then, I will unveil and exploit the existence of multiple correlations between the nature of doping ions and the energetics of apatitic phases, in view of deriving the energetic contribution of Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+} ions in an apatitic matrix (thereby extending the *ThermAP* model to these ions). I finally use these findings to draw, for the first time, estimates of the heat of formation, Gibbs free energy of formation and entropy of Ni , Co , Mn(II) and Fe(II) doped apatites; and some illustrative examples of the use of such data are given.

2. Materials and methods

2.1. Summary of the ThermAP additive model applied to phosphate apatites

The aim of this section is to recall the main aspects of the "predictive thermodynamic model" *ThermAP* that was developed recently for evaluating and understanding the energetics of phosphate apatite compounds: the full concept has been explained in detail elsewhere [1,5] and will thus only be overviewed here.

When (reliable) experimental data are available, these should of course be considered in priority for solving any thermodynamics related question. The problem arises when *no experimental data* is accessible for a given composition of interest. In this case, the best approach then lies in estimating this lacking information. In the case of apatites, several "predictive" methods have been tested [1], including the Volume Based Thermodynamics approach (VBT) developed in the literature for investigating other solid systems [20,21] as well as some additive contributional models. The VBT approach was found to be interesting but limited, in the case of apatites, by the fact that compositions with alkali earth cations had a clearly distinct behavior as compared to other divalent cations. In contrast, an additive model proved to be more "universal" and well adapted to estimate (within less than 1% of relative error, and often less than 0.5%) the energetics of phosphate bearing apatite compounds involving not only alkali earth cations (i.e. in the "s block" of the periodic chart of elements) but also cations from the "d block" (Cu, Zn, Cd) and in the "p block" (Pb).

This "predictive model" was elaborated from a thorough comparative analysis of experimental datasets accessible in the literature about 33 phosphate apatite end members involving the following ions: Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, PO_4^{3-}, HPO_4^{2-}, OH^-, F^-, Cl^- and/or Br^-. It is based on a simple "additive" concept, stating that the energetics (e.g. ΔH_f° or ΔG_f°) of a complex oxide are directly related to the energetics of the constituting binary oxides/compounds (e.g. CaO, P_2O_5 and CaF_2 in the case of fluorapatite $Ca_{10}(PO_4)_6F_2$) *provided that a corrective factor is applied on each contribution*. This type of additive model was previously used for evaluating the thermodynamics of other types of solids such as zeolites, simple phosphates or silicates [22 27]. Generally speaking, by considering a family or sub family of compounds, it becomes possible to constrain the corrective factors to be applied in this additive model. In practice, this refinement is undergone by finding the best fit between the values of ΔG_f°, ΔH_f° or S° calculated by the model and experimental ones, using a solver approach.

The concept of such corrective factors is by itself easy to catch: the energetic contribution of a given ion, e.g. Ca^{2+} for example, is likely to be rather similar for solids presenting the same crystalline structure (in the present case, the apatite structure). Using such an

TABLE 1
Contributive energetic values in the *ThermAP* predictive model, for the estimation of ΔG_f°, ΔH_f° or S° of phosphate apatites (at T = 298 K, 1 bar) from their composition (reproduced with permission from Drouet, JCT 2015 [1]). The relative uncertainty associated to each contribution is of the order of 1%.

Contributing sub-units in the apatite formula (T = 298 K, 1 bar)	g_i/(kJ · mol $^{-1}$)	h_i/(kJ · mol $^{-1}$)	s_i/(J · mol $^{-1}$ · K $^{-1}$)	Contribution to the oxygen stoichiometry
		Energetic contributions per divalent cation		
Ca^{2+}	−740	−790	38.8	1
Sr^{2+}	−740.9	−796.1	53	1
Mg^{2+}	−634.3	−666.4	23.1	1
Ba^{2+}	−739.4	−791.9	71.1	1
Cu^{2+}	−134.6	−171	34.6	1
Cd^{2+}	−262.4	−317	53.6	1
Pb^{2+}	−236.2	−282.2	81	1
Zn^{2+}	−344.5	−394.8	52.4	1
		Energetic contributions per anion		
PO_4^{3-}	−816.15	−861.6	41.05	2.5
OH^-	−140.8	−121.5	80.65	−0.5
F^-	−269.5	−237.2	68	−0.5
Cl^-	−103.5	−70	95.7	−0.5
Br^-	−90.5	−58	118.3	−0.5
		Energetic contributions for other species		
H^+	−147.75	−187.85	66.2	
H_2O (hydration)	−234	−290	50.7	
P_2O_5	−1632.3	−1723.2	82.1	

additive model, the contributions of various ions were recently evaluated for phosphate apatite compounds [1,5], with an appre ciable fit to experimental data (typically with mean relative errors less than 1% and often less than 0.5%, as mentioned above). In this case of phosphate apatites, table 1 summarizes these contributions in terms of enthalpy of formation, Gibbs free energy of formation and entropy, as reported previously [1].

Therefore, the *ThermAP* model (for which additive contributions are given in table 1) was established by determining the energetic contributions (in enthalpy or free energy or entropy) of ions once contained in a solid apatitic matrix. These contributions were eval uated by comparison to experimentally available data on several substituted apatites using a solver type of approach (multifactorial resolution of equations). In a first stage, the contribution of each ion was initially set to the enthalpy (or free energy or entropy respectively) of the related binary oxide. For a given apatite com position, this led to a rough estimate of the ΔH_f° (or ΔG_f° or S°) of the apatite compound. In a second step, these rough estimates were then corrected (by a multiplying corrective factor of the bin ary oxide energetics) so as to minimize the difference between estimates and experimental values. This minimization was made possible by solving a multi equation mathematical system (an equation providing from each apatite composition available exper imentally). The final set of energetic contributions found for each ion tested so far is reported in table 1. For example, as shown in table 1, the Gibbs contribution g_i of one calcium ion in a phosphate apatite compound, denoted g_{Ca}, is 740 kJ/mol. This value corre sponds, in this additive concept, to the contribution of one calcium ion to the Gibbs free energy of formation ΔG_f° of the considered apatite compound. When compared to the free energy of formation of the binary oxide involving calcium, namely CaO ($\Delta G_f^\circ(CaO)$ = 603.1 ± 0.9 kJ/mol [28]), one can see that the correcting factor $a_{corr,G,Ca}$ = 740/603.1 = 1.22(7) has to be applied to the free energy of CaO to find the Gibbs contribution of one calcium ion in apatite: $g_{Ca} = a_{corr,G,Ca} * \Delta G_f^\circ(CaO)$. Then, taking for example the case of fluo rapatite, $Ca_{10}(PO_4)_6F_2$, the application of the model leads to $\Delta G^\circ_{f\,estimated} = 10 * g_{Ca} + 6 * g_{PO4} + 2 * g_F$ = 12835.9 kJ/mol, and in a similar way to $\Delta H^\circ_{f\,estimated}$ = 13,544 kJ/mol and $S^\circ_{estimated}$ = 770.3 J mol^{-1} K^{-1}, which are in good agreement (within 1%) with the recommended experimental based values: ΔG_f° = 12,899 kJ/mol, ΔH_f° = 13,658 and S° = 778 J mol^{-1} K^{-1} (see experimental values compiled and discussed in reference [1]).

In a more formal way, this additive model can thus be described via a linear combination of the energetics of the constituting binary oxides/compounds. Thereafter, the energetics of an apatite com pound $M_{10}(PO_4)_6X_2$ (or a more complex solid solution. . .) is treated as the linear combination of the energetics of the constituting bin ary compounds MO, P_2O_5, and MX_2. For ΔH_f° and ΔG_f°, in particular, this gives:

$$\Delta H_f^\circ(complex\ oxide) \quad \sum_i v_i(a_{corr,H_i}\,\Delta H_f^\circ(binary\ oxide)),$$

$$\Delta G_f^\circ(complex\ oxide) \quad \sum_i v_i(a_{corr,G_i}\,\Delta G_f^\circ(binary\ oxide)),$$

where v_i represents the stoichiometry coefficient for the ion *i* found in a given chemical formula, and where $a_{corr,H}$ and $a_{corr,G}$ are the respective corrective factors.

This model has the advantage to allow estimating, at least in a first good approximation, thermodynamic data not available in the literature, especially for solid solutions of any complex composi tion as well as for non stoichiometric systems, as was also shown previously [1].

2.2. Methodology used in this work for extending the ThermAP model to nickel, manganese, iron and cobalt divalent ions

The above recapitulated model was initially established thanks to comparisons between calculated values and experimental data reported for apatite end members involving the cations Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+}. The present contribution focuses on the possible extension of this model to other divalent cations of potential applicative interest, namely Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+}. With this objective in mind, a methodology was thus followed, in two steps:

First, the energetic contributions obtained with the model for Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} cations were re examined for underlining some correlations between physico chemical characteristics of these ions and the overall ener getics (ΔG_f°, ΔH_f°) of the related apatite end members.

Second, after discussion the plausible reliability of extending such correlations to the cases of nickel, cobalt, manganese and iron, these correlations were exploited to evaluate the energetic contri butions of the latter in an apatite structure.

3. Results and discussion

3.1. Evaluation of the energetic contributions h_i and g_i of Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+} in phosphate apatites, based on the ThermAP additive model

The energetic contributions of Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} cations in an apatitic setting have been listed, using the *ThermAP* approach, in along with the energetics of the corre sponding binary oxides (typically from thermodynamic databases such as reference [28]) and the "corrective" factors as defined in the previous section. One observation is that the contributions h_i and g_i for the divalent cations M^{2+} tested are more negative than the value characteristic of the corresponding binary oxide MO.

TABLE 2
Energetic contributions of Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} divalent cations in a phosphate apatite matrix (*ThermAP* model, from Drouet, JCT 2015 [1]), and comparison to the corresponding binary oxides.

Ion	Enthalpy			Gibbs free energy			Thermo data
	Enthalpy contribution[a] h_i(kJ/mol)	ΔH_f° of binary oxide(kJ/mol)	Corrective factor $a_{corr,H}$	Gibbs free energy contribution$*g_i$(kJ/mol)	ΔG_f° of binary oxide(kJ/mol)	Corrective factor $a_{corr,G}$	Ionic radius[b] r_{ion} (Å)
Ca^{2+}	−790	−635.1	1.244	−740	−603.1	1.227	1
Sr^{2+}	−796	−592	1.347	−740.9	−561.9	1.319	1.16
Mg^{2+}	−666.4	−601.6	1.108	−634.3	−569.3	1.114	0.72
Ba^{2+}	−791.9	−548.1	1.445	−739.4	−520.4	1.421	1.36
Cu^{2+}	−171	−156.1	1.096	−134.6	−128.3	1.049	0.73
Cd^{2+}	−317	−258.4	1.227	−262.4	−228.7	1.147	0.95
Pb^{2+}	−282.2	−219	1.289	−236.2	−188.9	1.250	1.18
Zn^{2+}	−394.8	−350.46	1.127	−344.5	−320.52	1.075	0.745

[a] Contribution to the energetics of the considered apatite phase.
[b] Effective ionic radii (coord. 6) from Shannon and Prewitt, reference [31].

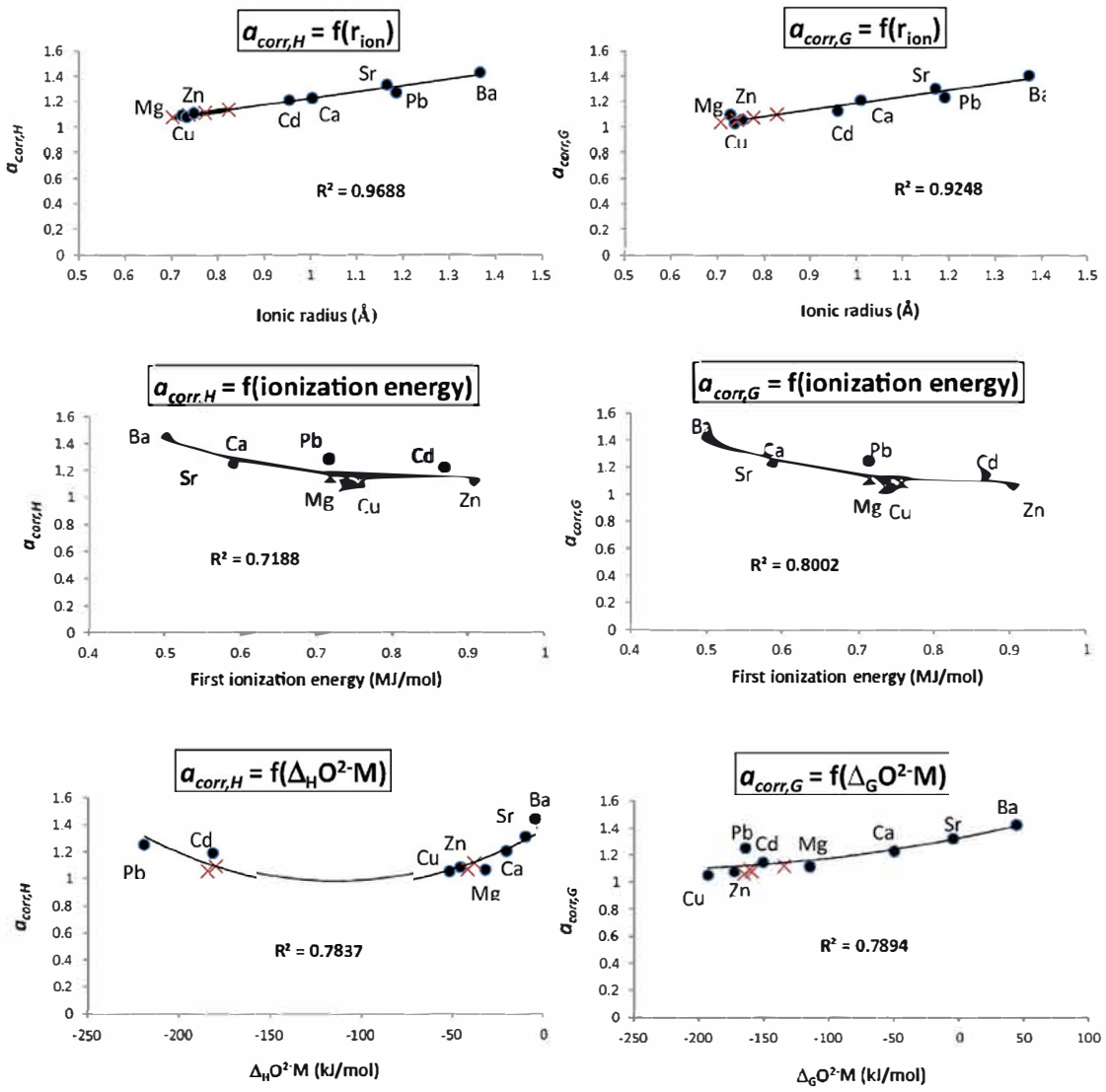

FIGURE 1. Identification of correlations between the corrective factors $a_{corr,H}$ and $a_{corr,G}$ (for divalent cations in phosphate apatites) and the corresponding ionic radius (r_{ion}), the first ionization energy, $\Delta_H O^{2-}M$ and $\Delta_G O^{2-}M$. Dark circles (●) represent divalent ions data treated in reference [1] and crosses (×) represent the additional ions Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+} treated in the present work.

This indicates that the ion in the apatitic array is more stable than in the corresponding binary oxides. In the same kind of idea, a negative value of experimental enthalpies of formation calculated "from the oxides" (and not from the elements in their standard state) has been noticed for apatitic compounds, whether in the case of non stoichiometric nanocrystalline apatites [29] or for lanthanide doped apatites [30].

It may be noted that the ions considered in this table are located in very distinct places in the periodic chart of elements, in the "s", "d" or "p" blocks. At this point, it was thus interesting to look for possible correlations versus specific features of these very diverse ions. In particular, the plots of $a_{corr,H}$ or $a_{corr,G}$ versus the effective ionic radius r_{ion} (taken from Shannon and Prewitt reference work [31], data for coordination number 6), can reasonably well be

TABLE 3
Energetic contributions evaluated in the present work for Mn^{2+}, Fe^{2+}, Ni^{2+} and Co^{2+} ions in phosphate apatites.

Ion	Enthalpy			Gibbs free energy			Entropy	Thermodata
	Estimated enthalpy contribution[a] h_i (kJ/mol)	ΔH_f° of binary oxide (kJ/mol)	*Estimated* corrective factor $a_{corr,H}$	*Estimated* Gibbs free energy contribution[a] g_i (kJ/mol)	ΔG_f° of binary oxide (kJ/mol)	*Estimated* corrective factor $a_{corr,G}$	*Estimated* entropy contribution s_i (J · mol $^{-1}$ · K $^{-1}$)	Ionic radius[b] r_{ion} (Å)
Ni^{2+}	−262.9	−239.3	1.099	−221.8	−211.1	1.051	38.6	0.7
Co^{2+}	−266.9	−237.9	1.122	−227.7	−214.1	1.063	53.3	0.735
Mn^{2+}	−446.8	−385.2	1.160	−403.6	−362.9	1.112	60.7	0.82
Fe^{2+}	−308.5	−272	1.134	−273.2	−251.4	1.087	61.3	0.77

[a] Values estimated in this work from the $a_{corr,} = f(r_{ion})$ linear correlations, see text.
[b] Effective ionic radii (coord. 6) from Shannon and Prewitt, reference [31]; high-spin (HS) radii were considered when applicable.

described by linear fits, with $R^2 = 0.9688$ and 0.9248 respectively, as shown in figure 1. Interestingly, the ions are well distributed along the line, independently of their position in the periodic classification of elements. The variation of these corrective factors versus other parameters was also tentatively followed. In particular, a respectable quadratic correlation ($R^2 \sim 0.7$ to 0.8) was found versus the first ionization energy of the elements (data from reference [32]). This datum, referring to the easiness of removing one electron from a given atom, is indeed related to the relative attraction of the nuclei for peripheral electrons and can thus be considered for understanding energetic phenomena. Another correlation was sought versus the parameters $\Delta_H O^2$ M or $\Delta_G O^2$ M, proposed by Tardy and collaborators [24,33] to describe differences between the energetics of binary oxides and of the corresponding aqueous ions. Again, a quadratic relationship (with $R^2 > 0.78$) could be identified.

The existence of such clear correlations between physico chemical parameters of the cation M^{2+} in phosphate apatite and their energetics (enthalpy and Gibbs free energies of formation) strongly supports, again, the use of this additive model for thermodynamic explorations of apatites, especially when no experimental data are available.

On the basis of these correlations, and keeping in mind that they were obtained for very diverse divalent ions (from either the "s", "p" or "d" block) of the periodic chart of elements, it then became appealing to extrapolate the energetic contributions of other divalent ions. As mentioned above, particular interest is found for 4 additional divalent cations of transition metals: Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+}. With this objective, the $a_{corr} = f(r_{ion})$ relationships determined here both for enthalpies and Gibbs free energies were used to evaluate the corrective factors $a_{corr,H}$ and $a_{corr,G}$ corresponding to these 4 new ions. The obtained values are tabulated in table 3 along with the energetics of the corresponding binary oxides (data from reference [28]), as well as the resulting contributions h_i and g_i for these 4 ions. It may be noted that the electronic structure of Mn(II), Fe(II) and Co divalent ions allows either high spin (HS) or low spin (LS) configurations, and the ionic radius is known to depend on the configuration. However, the calcium Ca(1) and Ca(2) sites in apatite are typically coordinated with OH^-, O^2 , F , Cl ... which are known to be low field ligands; in these conditions only the high spin configuration is suspected to occur in apatites [10]. Therefore, the HS ionic radii values were considered for the construction of table 3.

Again, these estimated contributions are more negative than the energetics of the binary oxides, indicating that for these ions as well, chemical environments in the apatitic structure are energetically favorable as compared to simple oxides. It is important to remark also that the two other correlations pointed out on figure 1 continue to be valid for the Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+} cations (indicated by cross marks), thus corroborating these values. Moreover, contributions of the same order of magnitude although not identical due to different chemical environments were also found for Fe^{2+}, Ni^{2+} and/or Co^{2+} in additive models reported by Chermak *et al.* [27] and La Iglesia [23], respectively for silicates and simple phosphates.

This estimation of energetic contributions h_i and g_i for Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+} ions in phosphate apatites, using the *ThermAP* approach, now theoretically allows one to evaluate the standard enthalpy of formation ΔH_f° and Gibbs free energy of formation ΔG_f° (from the elements taken in their standard state), at $T = 298$ K, for any phosphate apatite composition containing cations among Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+} and anions among OH , F , Cl and Br . Consequently, the knowledge of both ΔH_f° and ΔG_f° could then also lead to an estimation of entropy. However, as was mentioned previously [1], the propagation of errors (relative errors of the order of 1%) from such estimated ΔH_f° and ΔG_f° to entropy could lead to non negligible uncertainties. Therefore, it is generally a more recommended approach to estimate first entropies by a parallel method, and to combine it to ΔH_f° (or ΔG_f°) predicted by the *ThermAP* approach (unless known experimentally) to finally reach ΔG_f° (or ΔH_f° respectively), thus leading to a more reliable and self consistent set of $\Delta H_f^\circ/\Delta G_f^\circ/S^\circ$ values (i.e. obeying the law $\Delta G_f^\circ \quad \Delta H_f^\circ \quad T * \Delta S_f^\circ$).

For information, it can be added here that comparisons of calculated data using this model to existing experimentally available data on various compounds incorporating phosphate and $Ni^{2+}/Co^{2+}/Mn^{2+}/Fe^{2+}$ has been performed, for stressing the validity of this *ThermAP* approach even beyond purely apatitic compounds. Although differences are expected due to this "non apatitic" nature, a very good accord is found (typically with relative errors $\leqslant 2\%$), substantiating the validity of the model (see Supplementary Information, figure S1). Considering what was previously observed systematically for other cations using the *ThermAp* approach, and the comparative data of figure S1 for non apatitic compounds (for which a greater error is expected), then the estimated relative errors on the corrective factors a_{corr} and on g_i and h_i energetic contributions are expected to be lower than 2%.

The following section will first examine the question of the entropy, and will then combine entropy and enthalpy evaluations to derive Gibbs free energies, with the objective to ultimately propose self consistent thermodynamic estimates for Ni , Mn(II) , Fe(II) or Co apatites.

3.2. Entropy evaluations and derived considerations

Entropies or heat capacities have only rarely been determined for apatitic systems (see a compilation in reference [1]); therefore methods are needed to approximate them for unknown systems. The *ThermAP* approach proved to allow such evaluations, but to this day only for apatite compositions involving the ions Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^2, OH , F , Cl or Br (including solid solutions or non stoichiometric samples) for which some entropy values had been reported in the literature. But in the case of Ni^{2+}, Co^{2+}, Mn^{2+} or Fe^{2+} ions, no experimental values seem to be accessible. In this context, other estimation methodologies have thus to be utilized to evaluate entropies.

In reference [1], Drouet tested two additional approaches: (1) a Volume Based Thermodynamic (VBT) method, and (2) a method based on a comparison to the sum of entropies of the constituting binary compounds. VBT is an approach developed by Glasser and Jenkins (see for example [20,21]) for application to various types of systems. In a few words, this approach uses the fact that many physical characteristics of a solid, including its entropy, can be rather straight forwardly related to the volume "V_m" occupied by one unit formula. When applied to apatites with V_m ranging between 500 and 700 Å^3, a linear $S^\circ(\text{apatite}) = f(V_m)$ correlation was established [1], in first approximation. However, if considering for example the nickel, manganese (II), cobalt, or iron (II) hydroxyapatite end member compositions, i.e. $M_{10}(PO_4)_6(OH)_2$ with M = Ni, Mn(II), Co or Fe(II), the evaluated values of V_m go down to 382 Å^3 and thus fall significantly away from the 500 to 700 Å^3 range, making the previous correlation probably inaccurate for these 4 additional ions.

The second approach tested and discussed previously by Drouet [1] led to the approximated relationship: $S^\circ(M_{10}(PO_4)_6X_2) \cong 1.0428 * \sum_S$, where $\sum_S$ represents the sum of entropies of the corresponding binary compounds: $9\ MO + 3\ P_2O_5 + 1\ MX_2$. This

TABLE 4
Recommended thermodynamic data (at T = 298 K, 1 bar) for $Ni_{10}(PO_4)_6(OH)_2$, $Co_{10}(PO_4)_6(OH)_2$, $Mn_{10}(PO_4)_6(OH)_2$ and $Fe_{10}(PO_4)_6(OH)_2$ theoretical end-members.

Theoretical apatite end-member composition	Recommended thermodynamic values			
	Estimated[a] entropy $S°$ (J · mol $^{-1}$ · K $^{-1}$)	Derived entropy of formation from the elements $\Delta S_f°$ (kJ · mol $^{-1}$ · K $^{-1}$)	Estimated[b] enthalpy of formation from the elements $\Delta H_f°$ (kJ/mol)	Estimated[c] Gibbs free energy of formation from the elements $\Delta G_f°$(kJ/mol)
$Ni_{10}(PO_4)_6(OH)_2$	806	−2.537	−8042	−7286
$Co_{10}(PO_4)_6(OH)_2$	941	−2.403	−8082	−7366
$Mn_{10}(PO_4)_6(OH)_2$	1021	−2.342	−9880	−9182
$Fe_{10}(PO_4)_6(OH)_2$	1024	−2.292	−8498	−7815

[a] Estimated by applying the previously determined relationship $S°(M_{10}(PO_4)_6X_2) \cong 1.0428 * \sum_S$ (where $\sum_S$ is the entropy sum for binary compounds 9 MO + 3 P_2O_5 + 1 MX_2).
[b] Estimated in this work by extension of the *ThermAP* additive model.
[c] Estimated from application of $\Delta G_f°$ $\Delta H_f° - T * \Delta S_f$.

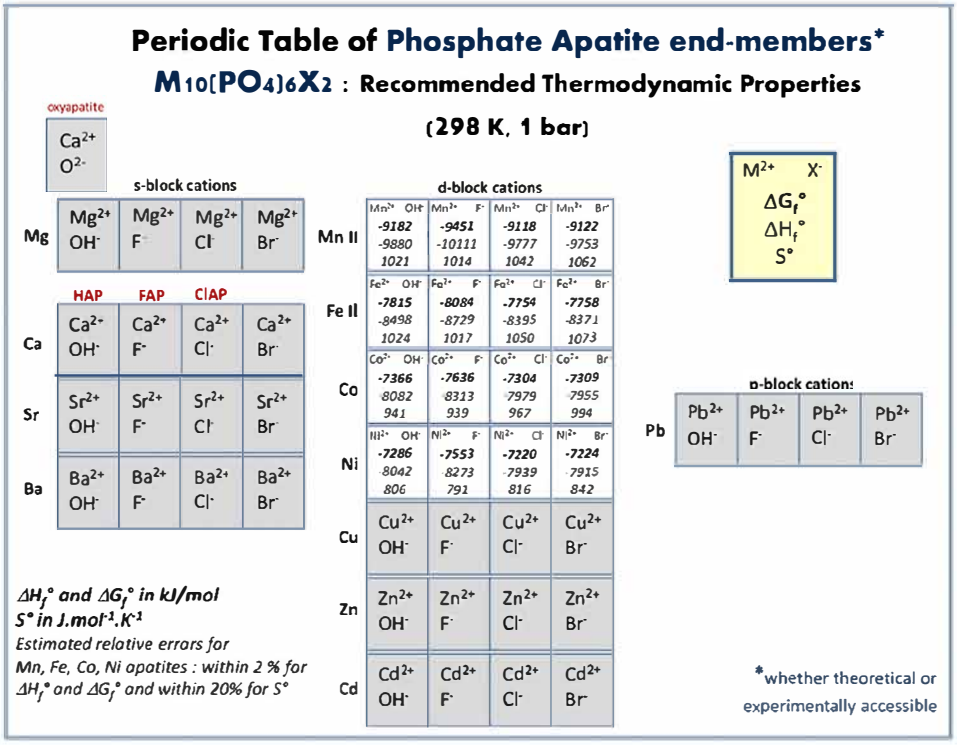

FIGURE 2. Periodic table summarizing recommended thermodynamic values (at T = 298 K, 1 bar), for theoretical $M_{10}(PO_4)_6X_2$ end-members with M = Ni, Co, Mn(II) or Fe(II) and X = OH, F, Cl or Br. The shaded zones have already been reported previously (see Table 5 in reference [1]) and therefore were not detailed here.

correlation was pointed out for values of $\sum_S$ in the range 750 to 1150 J mol $^{-1}$ K $^{-1}$. For more information on this result, please refer to the previously published paper (reference [1]). In the case of Ni , Co , Mn(II), or Fe(II) hydroxyapatite end members, the entropy sum $\sum_S$ for binary compounds lies for example between 770 and 980 J mol $^{-1}$ K $^{-1}$ (as calculated from reference [28]), thus contained in the previously considered range of 750 to 1150 J mol $^{-1}$ K $^{-1}$. Consequently, the previously determined linear like $S° \cong f(\sum_S)$ relationship may probably also be applied to the cases of nickel, cobalt, manganese (II) and iron (II). This leads to entropy values $S°$ (at T = 298 K) listed in the first column of table 4. Interestingly, rather similar values (within less than 3.5% of difference) are also found if estimating entropy from reactions of the type:

$$Ca_{10}(PO_4)_6(OH)_2 + 10NiO \rightarrow Ni_{10}(PO_4)_6(OH)_2 + 10CaO$$

and considering a change of entropy, $\Delta S°_{reaction}$, close to zero (as often approximated for reactions in the solid state for which the global variation of volume is small). This good accord thus supports the orders of magnitude found here for standard entropies $S°$ of the theoretical end member compositions $Ni_{10}(PO_4)_6(OH)_2$, $Co_{10}(PO_4)_6(OH)_2$, $Mn_{10}(PO_4)_6(OH)_2$ and $Fe_{10}(PO_4)_6(OH)_2$.

The enthalpy contributions h_i estimated in the previous section (see table 3) for Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+} allow the evaluation of the enthalpy of formation $\Delta H_f°$ of the above 4 end member compositions. Then, by combining $S°$ (in the form of the entropy of formation from the elements $\Delta S_f°$) and $\Delta H_f°$, the related Gibbs free energies of formation $\Delta G_f°$ can also be expressed thanks to the relationship $\Delta G_f°$ $\Delta H_f°$ $T * \Delta S_f°$. All these values have been added in table 4; they represent the best estimates to date for Ni , Co , Mn(II) or Fe(II) hydroxyapatite end members (whether theoretical or accessible by experiment).

If the same approach is carried out for the fluor , chlor or brom apatites series (considered at least theoretically), then it can similarly lead to the estimation of their standard thermodynamic properties. This has been done, and figure 2 gathers this information in the form of an easy to use periodic table of recommended thermodynamic data (shaded areas on this figure

correspond to previously published data [1] and were thus not reproduced here for the sake of clarity). In ref [1], it was shown that the *ThermAP* contributive approach was valid not only for OH but also F, Cl and Br, independently of the cations present. The validity of these estimations for F , Cl and Br bearing apatites can thus be reasonably expected.

The knowledge of S° for these end member compositions (whether theoretical or actually obtainable by experiment) also makes it possible to determine the entropy contributions "s_i" relative to the ions Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+} ions when incorporated in phosphate apatites. They can easily be obtained with the *ThermAP* approach by simply subtracting the contributions of the phosphate ion PO_4^{3-} and of the related monovalent anion X = OH , F , Cl or Br contained in the $M_{10}(PO_4)_6X_2$ formulas (for M = Ni, Co, Mn or Fe). The obtained s_i contributions for these 4 ions have thus been calculated and added in table 3. No experimental data on the entropy of Ni /Co /Mn /Fe apatites being available, entropies S° can however be tentatively estimated for other phosphate bearing compounds using the s_i contributions given in the present study in order to validate the order of magnitude of these data. This was performed with some metal phosphates (see Supplementary Information, figure S2). Despite the non apatitic nature of these compounds, the entropy estimated here for such metal phosphates have the same order of magnitude (with less than 20% of relative error) as experimental results. In the case of apatites, let's recall that maximal errors of up to 15% had been observed in some systems (see details on reference [1]). This arises from greater uncertainties on reported entropies as opposed to enthalpies or Gibbs free energies. However, since in the case of apatites the energetics are mostly driven by enthalpy rather than entropy (the enthalpy contribution is always clearly predominant for apatites as pointed out in reference [1]), then these comparisons allow considering the entropy contributions s_i estimated in the present manuscript as reasonably well fitted.

Such s_i values can prove helpful for evaluating with the *ThermAP* model the thermodynamic properties (ΔH_f°, ΔG_f° and S°) of apatite solid solutions or nonstoichiometric samples involving some amount of nickel, cobalt, manganese (II) or iron (II). Again, it is reminded that the recommended approach in this case (for limiting propagated errors) consists in *first* evaluating the entropy S° and the enthalpy ΔH_f°, by adding respectively the s_i and h_i contributions of the involved ions, and *then* to calculate the free energies ΔG_f° through $\Delta G_f^\circ \quad \Delta H_f^\circ \quad T * \Delta S_f^\circ$. For information, it can be remarked that the comparison of the ΔG_f° thus evaluated to values calculated directly from the g_i contributions (listed in tables 2 and 3) leads to an appreciable accord, with a mean relative error of 0.8%.

3.3. Some examples of uses and implications

As a graphical illustration of the above findings, figure 3 shows for example the evolution of ΔH_f° and ΔG_f° (at $T = 298$ K, 1 bar) for solid solutions between hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and respectively the end members $Ni_{10}(PO_4)_6(OH)_2$, $Co_{10}(PO_4)_6(OH)_2$, $Mn_{10}(PO_4)_6(OH)_2$ and $Fe_{10}(PO_4)_6(OH)_2$. It should be reminded here that these graphs do not imply "automatically" that all the members of these solid solutions can indeed be obtained by experiment; indeed a maximal limit of calcium substitution by nickel, cobalt, manganese (II) or iron (II) in hydroxyapatite may exist due to crystallographic or other constrains. However, several literature reports (see introduction section) have envisioned the possible incorporation of these ions, at least to some extent, in the apatitic structure. Any such composition accessible by the experiment will then have a given set of thermodynamic data which may be found in figure 3 (or in equivalent graphs for fluor , chlor apatites...).

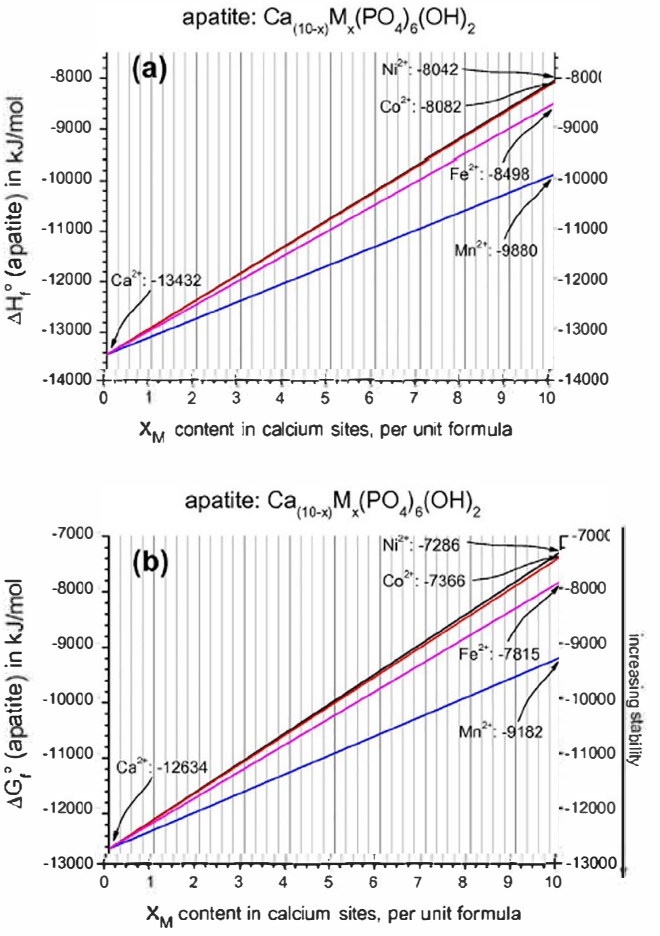

FIGURE 3. Graphical evolution of ΔH_f° (a) and ΔG_f° (b), for Ca-Ni-hydroxyapatite, Ca-Co-hydroxyapatite, Ca-Mn(II)-hydroxyapatite and Ca-Fe(II)-hydroxyapatite solid solutions (whether theoretical or obtainable by experiment).

In any case, the results obtained in the present contribution indicate that the following stability order can be evidenced (for a given amount of metal ion):

Mn(*II*)-apatite > Fe(*II*)-apatite > Co-apatite ⩾ Ni-apatite

with Cu apatite (studied previously [1], with $\Delta G_f^\circ \cong$ 6524 kJ/mol) being even less stable than nickel apatite. This stability ranking is not without remembering the order of the Mn, Fe, Co, Ni, Cu elements in Mendeleev's classification, however this cannot be "generalized" as, for example, Zn apatite stability (with a $\Delta G_f^\circ \cong$ 8623 kJ/mol [1]) remains between those of Mn(II) and Fe(II) apatites.

It may be remarked that in all additive models, the energetics of mixing is, by definition, neglected. Previous comments [1] however pointed out that the order of magnitude of enthalpies of mixing were extremely small (only a few tens of kJ/mol) compared to ΔH_f° or ΔG_f°, and in any case lower than the propagated uncertainty linked to the ΔH_f° and ΔG_f° estimates.

Another illustration of this work findings can for instance be found in the exploration of the energetics of precipitation reactions involving metal ions. Their precipitation in the form of apatitic solids has for example been proposed for the treatment of industrial waste waters; but what is the driving force of such reactions? Is this remediation route appropriate and energetically favorable? The knowledge of the energetics of apatites loaded with various metal ions now allows such questions to be answered. Let us consider, for example, the case of Ni^{2+} ions and their possible

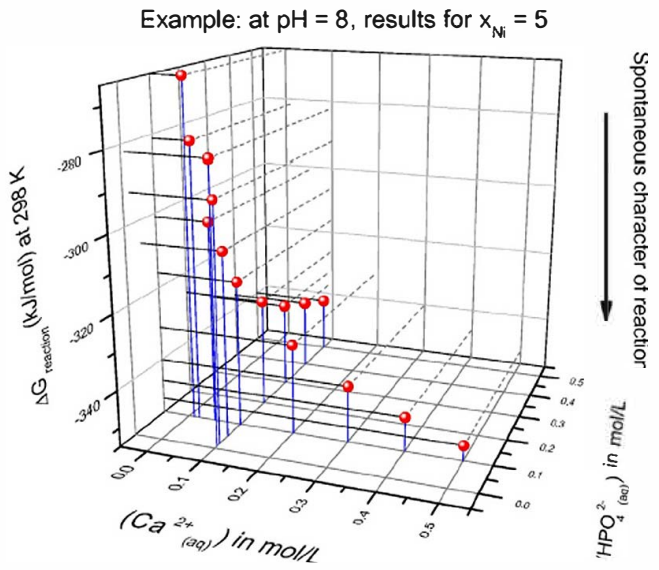

FIGURE 4. Example of evolution of $\Delta G_{reaction}$ (precipitation of nickel-doped hydroxyapatite $Ca_{(10-x)}Ni_x(PO_4)_6(OH)_2$) at pH = 8, for $(Ni^{2+}_{(aq)})$ = 0.2 M, and considering an "average" nickel amount of x = 0.5, versus calcium and hydrogenphosphate activities in solution (at 298 K).

precipitation in the form of a Ni doped calcium hydroxyapatite, at pH 8. This scenario can be described by the expected reaction:

$$(10-x)Ca^{2+}_{(aq)} + xNi^{2+}_{(aq)} + 6HPO^{2}_{4(aq)} + 8OH_{(aq)} \rightarrow Ca_{(10-x)}Ni_x(PO_4)_6(OH)_2 + 6H_2O_{(liq)}.$$

The calculation of the change in standard Gibbs free energy of reaction, $\Delta G°_{reaction}$, leads to values ranging from −686 to −541 kJ/mol for x increasing from 0 to 10. This shows the strong spontaneous character of this reaction at T = 298 K, in standard conditions. Then, in any given situation, it becomes possible to calculate the actual change $\Delta G_{reaction}$ from the relationship: $\Delta G°_{reaction} = \Delta G°_{reaction} + RT\,Ln(K)$ where K is the equilibrium constant of the reaction. Supposing for example a simple scenario with the following ionic activities in the medium $(Ca^{2+}_{(aq)})$ = 0.1 M, $(Ni^{2+}_{(aq)})$ = 0.2 M and $(HPO^{2}_{4(aq)})$ = 0.1 M, and a pH at 8, this would lead to values of $\Delta G_{reaction}$ between −321 and −215 kJ/mol, thus still energetically favorable. By calculating this amount for various values of ionic activities, the most appropriate conditions can then be searched. An example is given for illustrating this point on figure 4. In this case, one can see that increasing the amount of calcium and/or phosphate in solution, the $\Delta G_{reaction}$ value gets more and more negative (favorable situation). If the same plot is done for other nickel activities, on the other hand, $(Ni^{2+}_{(aq)})$ can be shown to leave almost unchanged $\Delta G_{reaction}$ which remains between −316 for 0.2 M of nickel and −301 for 0.001 M. Therefore, it is possible to use such calculations to identify the most crucial experimental parameters to modulate, and thus the best precipitation scenario to be used in a given industrial setting.

4. Concluding statement

The above example illustrated one possible use of the thermodynamic data reported in the present contribution; however the evaluation of energetic contributions of nickel, cobalt, manganese (II) or iron (II) doped apatites should now allow more numerous and precise thermodynamic calculations involving these phases, whether in natural settings (geochemistry, bone diagenesis...) or for applicative purposes. The general stability ranking Mn(II) apatite > Fe(II) apatite > Co apatite ≥ Ni apatite was established.

From a more general viewpoint, this work stresses again the interest of additive contributional approaches for the evaluation of unknown thermodynamic properties. Data for Ni^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+} ions obtained in the present work will therefore help enriching the apatite database of the *ThermAP* calculation sheet, freely accessible online (www.christophedrouet.com/thermAP).

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jct.2015.06.016.

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